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INTERNAL EXCHANGE IN NEW GROUP III

METALLOBORANE DERIVATIVES.

$(\text{CH}_3)_2\text{AlB}_3\text{H}_8$ AND $(\text{CH}_3)_2\text{GaB}_3\text{H}_8$

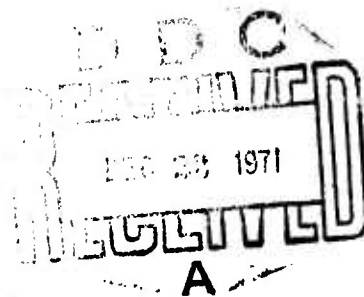
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Reaction of $(\text{CH}_3)_2\text{AlCl}$ and $(\text{CH}_3)_2\text{GaCl}$ with salts of the B_3H_8^- anion produces $(\text{CH}_3)_2\text{AlB}_3\text{H}_8$ and $(\text{CH}_3)_2\text{GaB}_3\text{H}_8$, respectively, in good yields. The nmr spectral characteristics are unusual and suggest several internal exchange processes.			

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Triborohydride						
dimethylaluminum triborane(8)						
dimethylgallium triborane(8)						
dimethylaluminum chloride						
dimethylgallium chloride						

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Internal Exchange in New Group III

Metalloborane Derivatives.

$(\text{CH}_3)_2\text{AlB}_3\text{H}_8$ and $(\text{CH}_3)_2\text{GaB}_3\text{H}_8$

Sir:

We wish to report the syntheses and preliminary structural studies of dimethylaluminum triborane(8) and dimethylgallium triborane(8).¹ Previously the chemistry of the B_3H_8^- anion² has been restricted to its use in the synthesis of higher boranes^{3,4} and transition metal complexes.^{5,6} The relatively recent development of convenient synthetic procedures^{3,7} makes this reagent potentially useful for a wide variety of chemical investigations, including the synthesis of covalent main group derivatives.

The preparation of $(\text{CH}_3)_2\text{AlB}_3\text{H}_8$ and $(\text{CH}_3)_2\text{GaB}_3\text{H}_8$ involves the reaction of $(\text{CH}_3)_2\text{GaCl}$ or $(\text{CH}_3)_2\text{AlCl}$ with salts of B_3H_8^- . In a typical reaction, excess NaB_3H_8 ² was stirred in a vacuum with 4.7 mmoles of solid $(\text{CH}_3)_2\text{GaCl}$ for 15 min. at room temperature, during which a mobile liquid was formed. The product $(\text{CH}_3)_2\text{GaB}_3\text{H}_8$ was then purified by high-vacuum fractional distillation; it distills slowly through a -45° trap and is essentially completely condensed by a -63° trap. The yield of purified $(\text{CH}_3)_2\text{GaB}_3\text{H}_8$ was 2.95 mmoles, 63%. The use of $(\text{CH}_3)_4\text{N}^+$, and $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ salts of B_3H_8^- produces similar yields of the product. The $(\text{CH}_3)_2\text{AlB}_3\text{H}_8$ was prepared

using the same procedures and similar yields were obtained. The volatilities of these compounds suggest that they are monomers, at least in the vapor phase. As their apparent thermal stability is marginal, vapor pressure measurements are not reliable purity criteria.

$(\text{CH}_3)_2\text{AlB}_3\text{H}_8$: 0° , 13torr; 19° , 35torr.

$(\text{CH}_3)_2\text{GaB}_3\text{H}_8$: 0° , 4torr; 24° , 13torr.

The gas phase infrared spectra of $(\text{CH}_3)_2\text{AlB}_3\text{H}_8$ and $(\text{CH}_3)_2\text{GaB}_3\text{H}_8$ are virtually identical in the stretching region, indicating that their vapor phase structures are probably very similar: $(\text{CH}_3)_2\text{AlB}_3\text{H}_8(\text{cm}^{-1} \pm 10)$; 2970(m), 2920(w), 2850(w), 2560(vs), 2510(s), 2200(vs). $(\text{CH}_3)_2\text{GaB}_3\text{H}_8$; 3050(sh), 2970(m), 2910(m), 2550(vs), 2480(s), 2140(vs).

Mass spectral studies have been complicated by the fact that both compounds polymerize at normal operating temperatures. Low temperature studies reduced the polymerization sufficiently to permit verification of the $(\text{CH}_3)_2\text{MB}_3\text{H}_x$ fragments, but the parent peak has not been observed (the same general problem was observed when 2,2- $(\text{CH}_3)_2\text{B}_4\text{H}_8$ was examined).⁴ The following parent group fragment ions were identified for $(\text{CH}_3)_2\text{GaB}_3\text{H}_8$.

$(^{12}\text{CH}_3)_2^{71}\text{Ga}^{11}\text{B}_3\text{H}_6$: found, 140.0474; Calcd., 140.0467.

$(^{12}\text{CH}_3)_2^{71}\text{Ga}^{11}\text{B}_3\text{H}_7$: found, 141.0548; Calcd., 141.0545.

The ^{11}B nmr spectra (32.0 MHz) of both new compounds are temperature dependent. At normal probe temperature (ca. 35°) the spectrum of $(\text{CH}_3)_2\text{GaB}_3\text{H}_8$ consists of a nine lined multiplet at $\delta 32.2 \pm 0.3$ ppm ($\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2 = 0.0$) with $J = 34 \pm 1$ Hz. These values are surprisingly similar to those obtained for the B_3H_8^- anion,⁸ except that the individual resonances are noticeably narrower in B_3H_8^- anion spectra. The spectrum of $(\text{CH}_3)_2\text{AlB}_3\text{H}_8$ is a slightly asymmetric singlet at $\delta 34.5$ ppm. At 50° the resonance is more symmetrical and somewhat narrower, and is shifted to $\delta 33.3$ ppm.

The ^1H nmr spectra (100 MHz) of the compounds are similar at normal probe temperature, consisting of a broad unresolved hump from the hydrogens on boron and a sharp singlet from the CH_3 groups. This data indicates that the CH_3 groups, boron atoms, and boron bound hydrogen are involved in rapid intramolecular exchange processes (on the nmr time scale) at room temperature.

An internal exchange mechanism has previously been proposed⁹ for the spectroscopically similar B_3H_8^- anion. Available ^{11}B nmr data indicate that the B_3H_8 moiety in $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_3\text{H}_8$ is involved in some exchange process,^{5,6,10} whereas in $[(\text{CH}_3)_4\text{N}][\text{Cr}(\text{CO})_4\text{B}_3\text{H}_8]$ it is not.⁶ Solid state structural studies of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_3\text{H}_8$ ¹¹ and $[(\text{CH}_3)_4\text{N}][\text{Cr}(\text{CO})_4\text{B}_3\text{H}_8]$ ¹² show that the previously determined B_3H_8^- anion structure is retained. In both $(\text{CH}_3)_2\text{GaB}_3\text{H}_8$ and $(\text{CH}_3)_2\text{AlB}_3\text{H}_8$, the ^{11}B nmr spectrum broadens as the temp-

erature is lowered and finally resolves into two resonances. In the case of $(\text{CH}_3)_2\text{GaB}_3\text{H}_8$, the smaller resonance is the broad hump at $\delta 12.9$ ppm, the larger resonance is a hump at $\delta 41.9$ ppm, and there is no visible fine structure. In the case of $(\text{CH}_3)_2\text{AlB}_3\text{H}_8$ however, the spectrum is somewhat better resolved, as is shown by the -23° example in Figure 1.

[Figure 1]

Crystal structures of metal- B_3H_8 systems^{11,12} show the bridging hydrogens of both B-H-B and B-H-M bonds to be closer to the borons near the metal, so the boron-bridge hydrogen bond lengths approximate those of boron-terminal hydrogens. Thus these borons are nearly equidistant from three hydrogens, which could account for the high field "quartet". It should be noted, however, that the "quartet" is slightly distorted and the intensity ratios are not ideal. The triplet would then be from the remaining boron split by its two terminal hydrogens, but not by the more distant bridge hydrogens. At temperatures below -23° the low-field resonance collapses to a broad singlet; the high field resonance also collapses, but with some ill-defined fine structure still visible.

The ^1H nmr spectral changes that occur as the temperature is lowered include three related phenomena. The boron bound hydrogens become somewhat magnetically differentiated. Nearly complete thermal decoupling¹⁰ is observed (some slight resonance narrowing occurs when ^{11}B double irradiation is applied), with at least four environments existing for boron

bound hydrogens below -90° . In addition, the CH_3 resonance is resolved below -70° into two equally intense peaks separated by 14 and 16 Hz, respectively, for $(\text{CH}_3)_2\text{GaB}_3\text{H}_8$ and $(\text{CH}_3)_2\text{AlB}_3\text{H}_8$.

Thus the low temperature nmr data appear consistent with static structures for $(\text{CH}_3)_2\text{AlB}_3\text{H}_8$ and $(\text{CH}_3)_2\text{GaB}_3\text{H}_8$ similar to the solid state structures of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_3\text{H}_8$ ¹¹ and $[(\text{CH}_3)_4\text{N}][\text{Cr}(\text{CO})_4\text{B}_3\text{H}_8]$ ¹², i.e. two adjacent B atoms of the B_3H_8 moiety are bound by the hydrogen bridge bonds, B-H-M, to the Al or Ga, (I). Equilibration of the CH_3 resonances at temperatures at which the B_3H_8 moiety is essentially static (~ 0 to -60°) may be envisioned as a result of cleavage of one of the B-H-M bridge bonds (II) followed by rotation of the $(\text{CH}_3)_2\text{M}$ group about the remaining B-H-M bridge, ($\text{I} \rightleftharpoons \text{II}$).

Methyl groups could also be equilibrated via a "flapping" motion; however, this seems unlikely considering the low temperatures at which the methyl groups are equivalent. At higher temperatures other exchange intermediates (III, IV, V) may also form in order to provide facile internal exchange routes ($\text{I} \rightleftharpoons \text{II} \rightleftharpoons \text{III}$, $\text{I} \rightleftharpoons \text{II} \rightleftharpoons \text{IV}$, $\text{I} \rightleftharpoons \text{II} \rightleftharpoons \text{V}$), for hydrogens around the B_3H_8 moiety while maintaining the CH_3 exchange.

[Insert mechanism here]

Further spectroscopic and chemical studies of these and related compounds are in progress.

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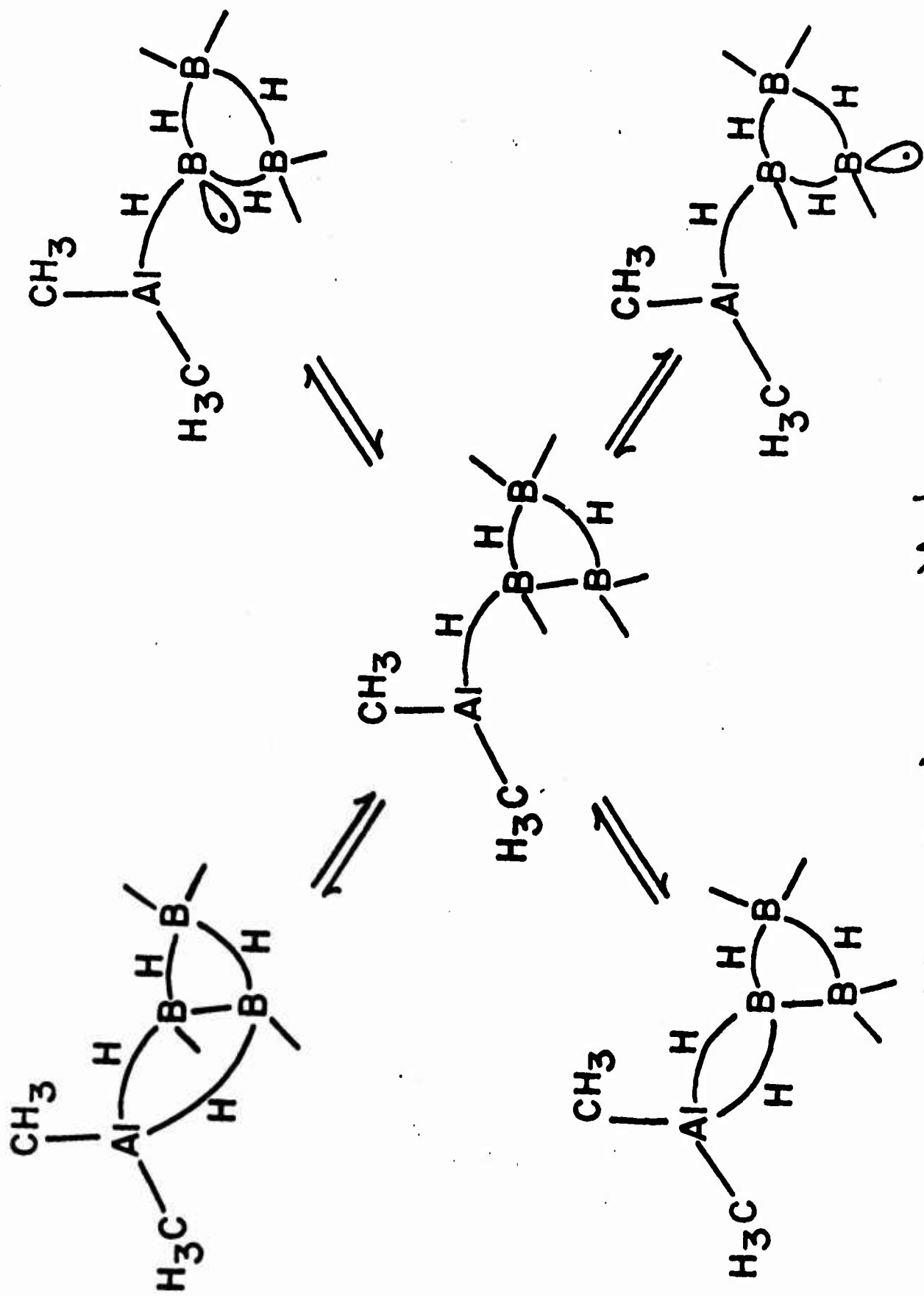
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### Figure Legend

Figure 1. The 32.1 MHz  $^{11}\text{B}$  nmr spectrum of  $(\text{CH}_3)_2\text{AlB}_3\text{H}_8$  at  $-23^\circ$ . Low field triplet:  $\delta = 14.0$  ppm and  $J = 125$  Hz, relative area 1.0. High field group:  $\delta = 41.4$  ppm and spacings of 78, 70 and 78 Hz, relative area 2.1.



Possible Exchange Mechanisms

$^{11}\text{B}$  NMR AT 32.1 MHz

$(\text{CH}_3)_2\text{AlB}_3\text{H}_8$

$-23^\circ$

100 Hz

$H_0 \rightarrow$

Figure 1.

## Abstract

The new group III borane compounds,  $(\text{CH}_3)_2\text{AlB}_3\text{H}_8$  and  $(\text{CH}_3)_2\text{GaB}_3\text{H}_8$ , are synthesized in good yield from the respective dimethyl group III chloride and  $\text{B}_3\text{H}_8^-$  salts. The  $^1\text{H}$  and  $^{11}\text{B}$  nmr spectra are temperature dependent: internal H exchange similar to that for the  $\text{B}_3\text{H}_8^-$  anion is apparent at elevated temperatures, while a static structure similar to that for the covalent transition metal  $\text{B}_3\text{H}_8$  derivatives is indicated at lower temperature.